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## DEGRADATION OF NATURAL ORGANIC MATTER IN WATER BY USING UV-C/H<sub>2</sub>O<sub>2</sub> PROCESS

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This laboratory study evaluated the ultraviolet (UV) photolysis, H<sub>2</sub>O<sub>2</sub> treatment and UV-C/H<sub>2</sub>O<sub>2</sub> advanced oxidation for the degradation of natural organic matter (NOM) in raw groundwater having high alkalinity and elevated dissolved organic carbon (DOC) concentration. The treatment efficiency was evaluated in terms of the reduction of DOC and UV absorbance at 254 nm (A<sub>254</sub>). UV photolysis and H<sub>2</sub>O<sub>2</sub> oxidation as standalone treatments were not effective at reducing DOC but the rate of DOC reduction increased markedly when H<sub>2</sub>O<sub>2</sub> was combined with UV-C radiation. At the optimal H<sub>2</sub>O<sub>2</sub> dose of 500 mg L<sup>-1</sup>, UV-C/H<sub>2</sub>O<sub>2</sub> treatment resulted in approximately 92% A<sub>254</sub> reduction and more than 83% DOC removal. Hydrogen carbonate and carbonate ions inhibited the degradation process.

**Key words:** natural organic matter, UV photolysis, UV-C/H<sub>2</sub>O<sub>2</sub> treatment.

**Razgradnja prirodnih organskih tvari u vodi primjenom UV-C/H<sub>2</sub>O<sub>2</sub> postupka.** Cilj ovog rada bio je istražiti primjenljivost izravne fotolize, vodikovog peroksida i UV-C/H<sub>2</sub>O<sub>2</sub> napredne oksidacije na razgradnju prirodnih organskih tvari u sirovoj bunarskoj vodi koju karakterizira visoki alkalitet i povišeni sadržaj otopljenog organskog ugljika (DOC). Učinkovitost obrade vrednovala se u pogledu smanjenja koncentracije DOC-a i UV apsorbancije pri 254 nm (A<sub>254</sub>). Primjenom izravne UV fotolize kao i oksidacije vodikovim peroksidom nije se postiglo smanjenje sadržaja DOC-a, ali se zato brzina smanjenja DOC-a znatno povećala pri oksidaciji uz istovremenu prisutnost vodikova peroksida i UV zračenja. Primjenom optimalne doze vodikova peroksida od 500 mg L<sup>-1</sup>, UV-C/H<sub>2</sub>O<sub>2</sub> postupkom ostvarilo se smanjenje A<sub>254</sub> od približno 92% i uklanjanje više od 83% početnog sadržaja DOC-a. Prisutnost hidrogenkarbonatnih i karbonatnih iona u vodi djeluje inhibitorno na postupak razgradnje.

**Ključne riječi:** prirodne organske tvari, UV fotoliza, UV-C/H<sub>2</sub>O<sub>2</sub> postupak.

## INTRODUCTION

The ubiquitous presence of NOM in surface and groundwater bodies causes a number of problems in drinking water treatment that include, *inter alia*, the deterioration of the organoleptic properties of water (color, taste and odor), the increase in the content of complexed heavy metals and adsorbed organic pollutants (e.g. pesticides), the increased use of coagulants

and disinfectants with a resulting increase in sludge and disinfection by-products (DBPs) formation, the reduction of the adsorption capacity of activated carbon, the clogging of the membranes followed by a rapid decline in permeate flux, and the stimulation of biological growth in the distribution system [1, 2].

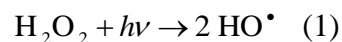
Before the 1970s, research and treatment methods for NOM removal were traditionally focused on the removal of color [3, 4]. After the discovery of organohalides in chlorinated drinking water in 1974 [5, 6], considerable research attention has been directed to the removal of DBP precursors, predominantly NOM. The concern over DBPs in chlorinated drinking water has triggered regulatory actions aimed at reducing the level of exposure to some DBPs without compromising the disinfection efficacy. Hence, to achieve compliance with the maximum contaminant level (MCL) for several regulated chlorination by-products, the public drinking water supply systems need to consider different approaches to limiting DBPs such as enhanced removal of precursor compounds present in raw water sources, the application of alternative disinfectants, or removing DBPs after their formation, which is a less viable option [7, 8].

The removal of organic precursors can be achieved by enhancing the existing coagulation-flocculation-sedimentation processes or by providing additional processes such as granular activated carbon (GAC) filtration and nanofiltration (NF). However, enhanced coagulation optimized for the removal of total organic carbon (TOC) as well as GAC filtration can reduce DBP precursors sufficiently, but not the bromide ion (an inorganic DBP precursor), resulting in an increased bromide to TOC ratio, which, in turn, causes a shift in the speciation of DBPs towards brominated by-products that are generally more carcinogenic and genotoxic than are chlorinated DBPs [9]. NF membranes, on the other hand, offer a relatively high bromide rejections, but still to a lesser extent than the rejections of DBP precursors. As a result, an elevated ratio of bromide to TOC will favor the formation of brominated species upon chlorination, but their concentrations in the

finished water will be very low [7, 8, 10, 11].

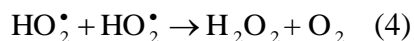
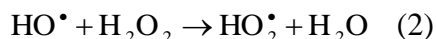
The use of alternative chemical disinfectants, such as ozone, chloramines and chlorine dioxide to minimize the formation of the two major classes of halogenated DBPs – trihalomethanes (THMs) and haloacetic acids (HAAs), also has certain limitations. Each of them has been shown to produce its own DBPs of health concern. For example, typical by-products of the chloramination process are THMs, HAAs and haloacetoneitriles (HANs); the major chlorine dioxide DBPs of concern are chlorite and chlorate, while aldehydes, ketones and carboxylic acids are commonly present in ozonated water. In addition, ozone is known to react directly or indirectly with bromide ions to form bromate [12].

Advanced oxidation processes (AOPs) are another treatment option that should be considered for the degradation of NOM. AOPs make use of hydroxyl radicals ( $\bullet\text{OH}$ ) that react non-selectively with organic molecules with reaction rate constants typically several orders of magnitude higher than those of common oxidants used in water treatment [1, 13-16]. Among the many AOPs, UV-C/H<sub>2</sub>O<sub>2</sub> process has become a standard advanced oxidation process for the reduction of a broad spectrum of trace organic contaminants and naturally occurring organic matter [17-20]. In the UV-C/H<sub>2</sub>O<sub>2</sub> process,  $\bullet\text{OH}$  radicals are formed by homolytic cleavage of the O-O bond in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) under UV-C irradiation:



Because the molar absorption coefficient of H<sub>2</sub>O<sub>2</sub> is quite low, 19.6 L mol<sup>-1</sup> cm<sup>-1</sup> at 254 nm [21], it is necessary to have a high concentration of H<sub>2</sub>O<sub>2</sub> in the reaction system to produce a sufficient concentration of  $\bullet\text{OH}$  radicals. Unfortunately, in the presence of an excess of H<sub>2</sub>O<sub>2</sub> the

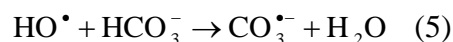
scavenging of •OH radicals occur, causing the process to be less effective [22]:



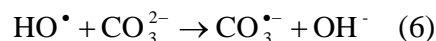
Thus, for a given reaction system there is an optimum H<sub>2</sub>O<sub>2</sub> dosage in the UV-C/H<sub>2</sub>O<sub>2</sub> process at which maximum removal of the target substance is achieved. Beltrán et al. [23] reported an optimum initial H<sub>2</sub>O<sub>2</sub> concentration of about 0.01 mol L<sup>-1</sup> above which the oxidation rate of atrazine decreased. Andreozzi et al. [24] also found a hydrogen peroxide dosage of 0.01 mol L<sup>-1</sup> as a value beyond which further additions were not effective for the oxidation of metol (*N*-methyl-*p*-amino-phenol) by UV/H<sub>2</sub>O<sub>2</sub> treatment. A study by Wang et al. [25] showed that the degradation rate of humic acid during the UV/H<sub>2</sub>O<sub>2</sub> process increased with the increase of hydrogen peroxide concentration up to 0.01% (2.94 mmol L<sup>-1</sup>) and then decreased with further increase in H<sub>2</sub>O<sub>2</sub> concentration.

Moreover, it is well known that hydrogen carbonate and carbonate ions (i.e.

alkalinity-contributing species) act as hydroxyl radical scavengers according to the following reactions [26, 27]:



$$k = 8.5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$$



$$k = 4.2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$$

The carbonate radical anion formed from the reactions between •OH radicals and inorganic carbon is a weaker oxidant than •OH, and generally more selective toward organic compounds [22, 26]. Since the carbonate system of natural waters (HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup>) efficiently scavenges hydroxyl radicals, it leads to a decrease in the steady-state concentration of •OH and thus affects the overall degradation efficiency.

This laboratory study aimed to assess the impact of a UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation on the removal of NOM from natural water containing elevated concentration of dissolved organic carbon (DOC) and high alkalinity. The treatment efficiency was evaluated in terms of the reduction of DOC and UV absorbance at 254 nm (A<sub>254</sub>).

## MATERIALS AND METHODS

### Water characterization

Groundwater samples were collected from a well in Županja, Croatia. This groundwater, pretreated by sand filtration, is planned to be used as a food ingredient in the local food-processing industry. Untreated groundwater is characterized by high alkalinity and elevated DOC concentrations with a high level of humic substances, as evidenced by the corresponding values of

specific UV absorbance at 254 nm (SUVA<sub>254</sub>). All the samples were filtered through a 0.1 μm prewashed cellulose nitrate membrane filter (Sartorius AG, Goettingen, Germany) and immediately stored in the dark before any measurements were made. The major physicochemical properties of the water are summarized in Table 1.

**Table 1.** Water quality parameters**Tablica 1.** Parametri kvalitete vode

Parameter	Value
pH	8.46
Conductivity ( $\mu\text{S cm}^{-1}$ )	866
Hardness ( $\text{mg L}^{-1}$ as $\text{CaCO}_3$ )	137
Alkalinity ( $\text{mg L}^{-1}$ as $\text{CaCO}_3$ )	405
$A_{254}$ ( $\text{cm}^{-1}$ )	0.271
DOC*, ( $\text{mg L}^{-1}$ )	4.68
SUVA <sub>254</sub> , ( $\text{m}^{-1} \text{L mg}^{-1}$ )	5.79
Bromide ( $\text{mg L}^{-1}$ )	0.28
Chloride ( $\text{mg L}^{-1}$ )	65.8
Fluoride ( $\text{mg L}^{-1}$ )	0.06
Nitrate ( $\text{mg L}^{-1}$ )	5.43
Sulfate ( $\text{mg L}^{-1}$ )	0.06
Phosphate ( $\text{mg L}^{-1}$ )	0.46
Calcium ( $\text{mg L}^{-1}$ )	32.9
Magnesium ( $\text{mg L}^{-1}$ )	13.4
Sodium ( $\text{mg L}^{-1}$ )	149.8
Potassium ( $\text{mg L}^{-1}$ )	0.89

## Chemicals and reagents

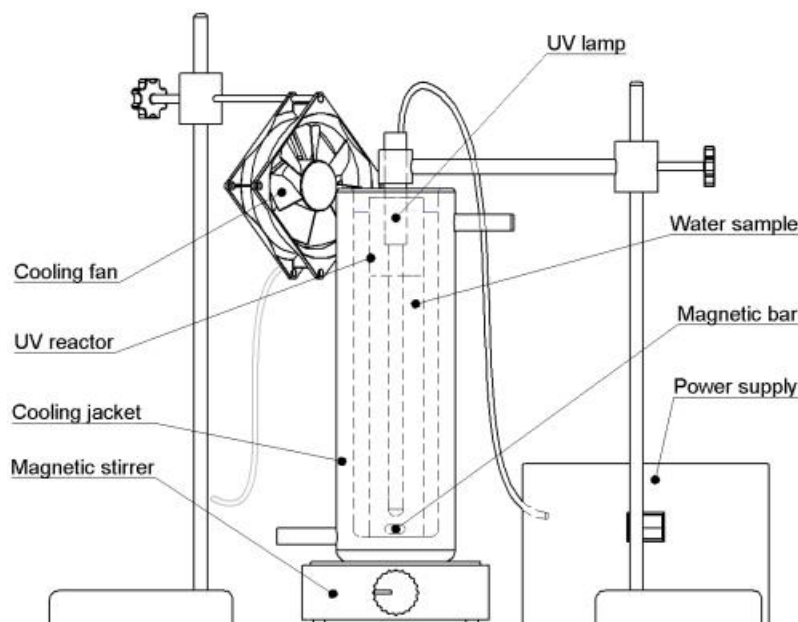
Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, w/w) used in the experiments was supplied by Kemika (Zagreb, Croatia). The required concentrations of  $\text{H}_2\text{O}_2$  solutions were prepared using ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}$

resistivity at  $25^\circ\text{C}$ ,  $< 5$  ppb total organic carbon) obtained from a GenPure ultrapure water system (TKA, Niederelbert, Germany).

## Experimental procedure

All experiments were carried out in a cylindrical glass reactor ( $D = 28 \text{ mm}$ ,  $H = 202 \text{ mm}$ ) filled up with 105 mL of reaction mixture. The radiation source was a UVP low pressure mercury vapor UV lamp placed in the center of the reactor, which emits primarily monochromatic light at 254 nm (model Pen-Ray 90-0012-01, UVP, Cambridge, UK) (Figure 1). The value of incident photon flux at 254 nm,  $1.03 \times 10^{-6} \text{ einstein s}^{-1}$ , was determined by hydrogen

peroxide actinometry following the procedure outlined in Nicole et al. [28]. The lamp was warmed up for at least 15 minutes prior to each experimental run. During the experimental time period of 180 minutes, the reaction temperature ( $25 \pm 0.5^\circ\text{C}$ ) was controlled by circulating cooling water through a jacket around the reactor and the reaction mixture was stirred with a magnetic stirrer at constant speed.



**Figure 1.** Schematic diagram of cylindrical batch reactor

**Slika 1.** Shematski prikaz cilindričnog šaržnog reaktora

Two initial types of experiments were carried out in order to investigate the separate influence of UV radiation and H<sub>2</sub>O<sub>2</sub> on the degradation of NOM in Županja water. One was conducted with a mixture of Županja water (100 mL) and H<sub>2</sub>O<sub>2</sub> (5 mL) with a total concentration of H<sub>2</sub>O<sub>2</sub> of 150 mg L<sup>-1</sup> and without UV radiation exposure. The other was carried out with UV radiation applied to Županja water (105 mL), but without adding hydrogen peroxide.

Samples for the UV/H<sub>2</sub>O<sub>2</sub> experiments were prepared by adding 100 mL of

Županja water and 5 mL of H<sub>2</sub>O<sub>2</sub> solution so that the final concentrations of hydrogen peroxide were 50, 100, 150, 200, 300, 400, 500, 600, 800 and 1000 mg L<sup>-1</sup>.

During each experimental run, small samples were taken for the absorbance measurement at the beginning and after 10, 20, 30, 60, 90, 120, 150, and 180 minutes. The pH value and the concentration of DOC (measured as NPOC) were determined at the beginning and at the end of each experiment.

## Analytical methods

All spectrophotometric measurements were made with an HP 8453 UV-Vis spectrophotometer (Hewlett Packard, USA) using a 1 cm quartz cell.

Dissolved organic carbon concentrations (measured as NPOC) were determined using a Shimadzu TOC-V<sub>CPH</sub>

total organic carbon analyzer (Shimadzu Corporation, Japan).

The concentrations of major cations and anions in groundwater were determined by ion chromatography using a Dionex ICS-3000 system (Dionex, Sunnyvale, CA). The separation of cations was performed under

isocratic conditions at 40 °C using a Dionex IonPac CS16 analytical column (250 × 5 mm i.d.) with the mobile phase containing 30 mM methanesulfonic acid (MSA) at a flow rate of 1 mL min<sup>-1</sup> and an injection volume of 10 µL. The separation of anions was achieved at 30 °C using a Dionex IonPac AS15 analytical column (250 × 2 mm i.d.) and isocratic elution with 0.035 mol L<sup>-1</sup> NaOH solution as mobile phase at a flow

rate of 0.36 mL min<sup>-1</sup>, with an injection volume of 10 µL.

Alkalinity and hardness were measured according to standard methods [29].

The temperature was controlled using a Testo 110 digital thermometer (Testo, Germany) and the pH value of the solutions was measured with a pH-meter (model Sevencompact pH/Ion S220, Mettler-Toledo International Inc.).

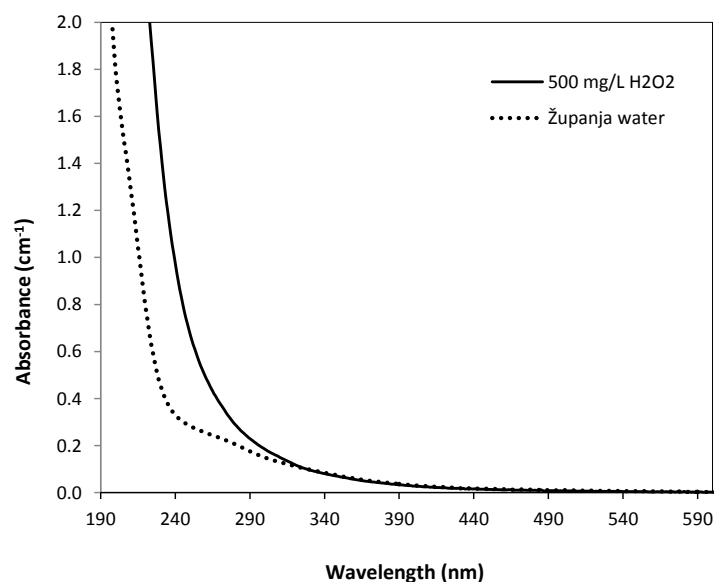
## RESULTS AND DISCUSSION

### Absorption of UV radiation in the reactor

Both H<sub>2</sub>O<sub>2</sub> and NOM molecules in water can absorb the radiation, but when exposed to UV radiation of wavelengths less than 300 nm, hydrogen peroxide becomes the dominant absorbing species (Figure 2). These observations are in agreement with those reported by Beltrán et al. [30], who concluded that H<sub>2</sub>O<sub>2</sub> is the main absorber when its concentration in wastewater with a lower organic load is higher than 0.01 mol L<sup>-1</sup>, and Wang et al. [25] who found that H<sub>2</sub>O<sub>2</sub> is the principal absorber of UV light in dilute

aqueous solutions of humic acid (~10 mg L<sup>-1</sup>), in the presence of hydrogen peroxide in the concentration range 0.001–0.5% (0.3–163 mmol L<sup>-1</sup>).

Since the absorption onset of H<sub>2</sub>O<sub>2</sub> molecule begins at 310 nm [31], UV radiation below this wavelength provides enough energy to the molecule to cleave the O-O bond and produce •OH radicals according to Eq. (1).



**Figure 2.** Absorption spectra of H<sub>2</sub>O<sub>2</sub> and NOM in Županja water

**Slika 2.** Apsorpcijski spektri H<sub>2</sub>O<sub>2</sub> i prirodnih organskih tvari u županjskoj vodi

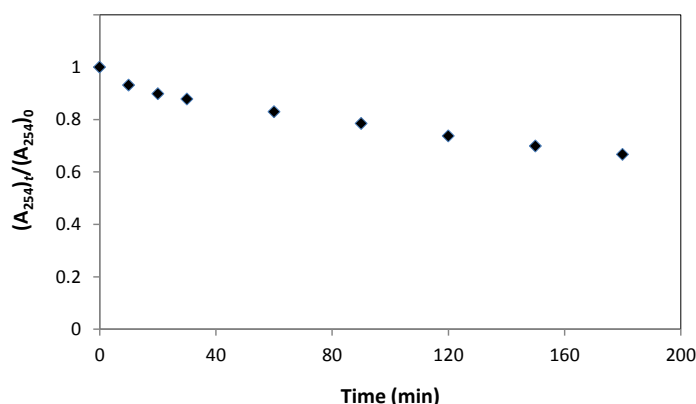


## Direct photolysis of NOM

Direct photolysis was first performed to isolate the effect of UV-C radiation at 254 nm on  $A_{254}$  and DOC reduction. The successful application of UV photolysis implies that the subject compounds have a high UV absorbance and a high quantum yield in order to be susceptible to photodegradation. The absorption spectrum characteristics of the absorbing species depend on the presence and type of specific molecular moieties called chromophores, which are responsible for the light absorption. Absorption of photons by chromophoric NOM molecules promotes them to a higher energy electronic state. The excited NOM chromophores may react further with dissolved molecular oxygen via

electron transfer to produce superoxide radical anion ( $O_2^{\bullet-}$ ) and radical cation, or may form carbon centered radicals via single bond homolysis that are subsequently trapped by molecular oxygen to form peroxy radicals ( $RO_2^{\bullet}$ ), which lead to an enhancement of the photodegradation process, and eventually to complete mineralization [26, 31].

In this study, the UV direct photolysis of NOM resulted in no significant change in DOC content and had only slight effect on the  $A_{254}$  reduction (33.4%). The reduction of UV absorbance at 254 nm is shown in Figure 3.



**Figure 3.** Reduction of UV absorbance at 254 nm during direct photolysis  
**Slika 3.** Smanjenje UV apsorbancije pri 254 nm tijekom izravne fotolize

It is obvious that UV direct photolysis is not effective as a standalone treatment for DOC removal and has only limited impact on  $A_{254}$  reduction. The lack of removal of DOC by direct UV photolysis can be attributed to the use of an inappro-

priate UV lamp and the presence of organic matter that are quite resistant to fragmentation. The optimization of photodegradation process by using UV lamps of different intensities and wavelength outputs was beyond the scope of this study.

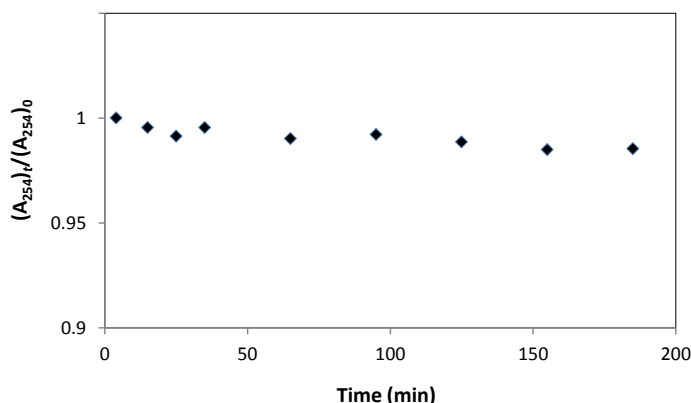
## Treatment with H<sub>2</sub>O<sub>2</sub> without UV radiation

As in the UV photolysis experiment, the treatment with H<sub>2</sub>O<sub>2</sub> failed to decrease

the concentration of DOC in groundwater. Moreover, the effect of the addition of 150

mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (4.4 mmol L<sup>-1</sup>) on the A<sub>254</sub> reduction was mainly negligible (Fig. 4). The strong oxidizing power of hydrogen

peroxide, with a reduction potential of 1.77 V, was not found to be sufficient to induce fragmentation of NOM molecules.



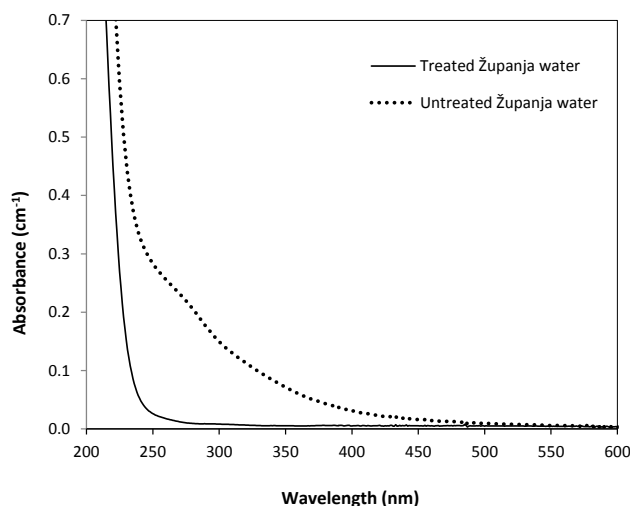
**Figure 4.** Reduction of UV absorbance at 254 nm in H<sub>2</sub>O<sub>2</sub> treatment without UV radiation

**Slika 4.** Smanjenje UV apsorbancije pri 254 nm u postupku s H<sub>2</sub>O<sub>2</sub> bez prisutnosti UV zračenja

#### UV-C/H<sub>2</sub>O<sub>2</sub> treatment

While H<sub>2</sub>O<sub>2</sub> alone was not effective in the removal of NOM, in combination with UV-C radiation the rate of the transformation and removal of NOM, measured indirectly as a decrease in UV absorbance at 254 nm and DOC concentration, increased significantly compared to direct photolysis. Obviously, the addition of hydrogen peroxide resulted in

the formation of •OH radicals generated by the photolysis of H<sub>2</sub>O<sub>2</sub>. This indicates that hydroxyl radicals play a dominant role in the degradation of NOM molecules. At the optimal H<sub>2</sub>O<sub>2</sub> dose of 500 mg L<sup>-1</sup> (14.7 mmol L<sup>-1</sup>) the A<sub>254</sub> reduction was greatly improved, with an overall reduction of about 92% (Fig. 5).



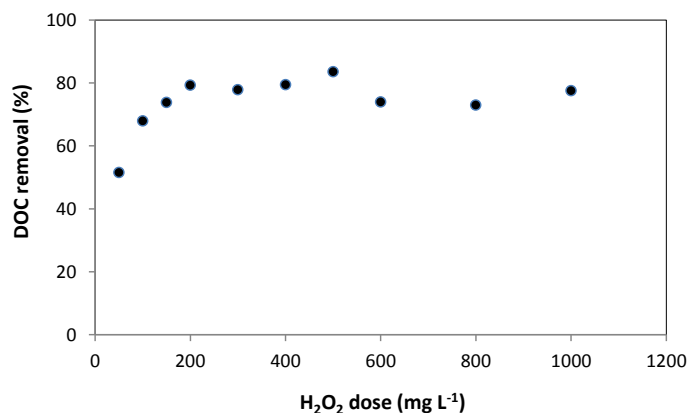
**Figure 5.** UV spectrum of Županja water before and after UV-C/H<sub>2</sub>O<sub>2</sub> treatment. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 14.7 mmol L<sup>-1</sup>

**Slika 5.** UV spektar županjske vode prije i nakon obrade UV-C/H<sub>2</sub>O<sub>2</sub> postupkom. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 14,7 mmol L<sup>-1</sup>



The highest DOC reduction, 83.5%, was achieved also using the optimal H<sub>2</sub>O<sub>2</sub> dose. The Figure 6 shows the effect of H<sub>2</sub>O<sub>2</sub>

concentration on DOC removal by UV-C/H<sub>2</sub>O<sub>2</sub> process.



**Figure 6.** Effect of UV-C/H<sub>2</sub>O<sub>2</sub> oxidation on DOC removal as a function of H<sub>2</sub>O<sub>2</sub> dose

**Slika 6.** Učinak UV-C/H<sub>2</sub>O<sub>2</sub> oksidacije na uklanjanje otopljenog organskog ugljika u ovisnosti o dozi vodikova peroksida

DOC removal increased with increasing H<sub>2</sub>O<sub>2</sub> dose up to 500 mg L<sup>-1</sup> and then decreased with further increase in H<sub>2</sub>O<sub>2</sub> concentration. This phenomenon occurs due to the scavenging of •OH radicals by H<sub>2</sub>O<sub>2</sub> itself (Equations 2–4), and leads to a decrease in NOM removal efficiency.

The optimal H<sub>2</sub>O<sub>2</sub> dose seems rather high compared to those observed by Goslan et al. [32] and Wang et al. [25]. The differences are likely due to the higher alkalinity of Županja water (405 mg L<sup>-1</sup> as CaCO<sub>3</sub>) where the scavenger species HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> affect the efficiency of NOM

removal by competition for •OH radicals (Equations 5 and 6). Since the pH governs the distribution of these species in water, at the pH of around 8.5, the dominant species is the hydrogen carbonate ion (HCO<sub>3</sub><sup>-</sup>). Although the rate constant for the reaction between •OH radicals and HCO<sub>3</sub><sup>-</sup> is approximately 49 times lower than that of CO<sub>3</sub><sup>2-</sup>, due to the high alkalinity of the water there is enough HCO<sub>3</sub><sup>-</sup> to cause scavenging effects. To improve the efficiency of this treatment, the addition of a pretreatment process for the removal of alkalinity need to be considered.

### Implications on water quality

Due to the long irradiation time and the high initial H<sub>2</sub>O<sub>2</sub> concentration, a high mineralization of NOM was achieved. The amount of NOM in water not removed by UV-C/H<sub>2</sub>O<sub>2</sub> treatment was subjected to structural change, as evidenced by the very low value of UV absorbance at 254 nm

(0.022 cm<sup>-1</sup>). However, the partial oxidation of NOM may lead also to increase in total trihalomethanes yield upon chlorination [33] and biodegradability of NOM [20]. This may have a negative impact on the stability and quality of water and a subsequent biological treatment may be required.

## CONCLUSION

The following conclusions can be drawn from this laboratory study:

- The UV direct photolysis of NOM resulted in no significant change in DOC concentration and had only slight effect on the A<sub>254</sub> reduction. This suggested that direct photolysis was not effective as a standalone treatment for DOC removal under the conditions used in the present study. Further research should take into account the use of UV lamps with different intensities and wavelength outputs to optimize the photodegradation process.
- After treatment with 150 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> for 3 h no significant changes were observed, either in DOC content or in the A<sub>254</sub>.
- At the optimal H<sub>2</sub>O<sub>2</sub> dose, UV-C/H<sub>2</sub>O<sub>2</sub> treatment resulted in approximately 92% A<sub>254</sub> reduction and more than 83% DOC removal.
- The observed high value of 500 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> for the optimal dose may be explained by the radical scavenging effects of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> anions due to the high alkalinity of the water.
- The results suggest that UV-C/H<sub>2</sub>O<sub>2</sub> advanced oxidation has great potential for the removal of NOM in Županja raw water but further research should aim at optimizing the process conditions, including NOM characterization and by-product identification.

## Acknowledgements

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